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学位論文の要約

題目　　Studies on Hydrogen-Storage Properties of Palladium Based Nanomaterials
（パラジウム基ナノ材料の水素吸蔵特性に関する研究）

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序論

Hydrogen energy is a clean and sustainable energy carrier. Pd is a well-known metal for hydrogen storage at room temperature. Compared to Pd bulk, Pd nanocrystals exhibit high surface atomic ratio and high catalytic activity in hydrogenation reaction. The purpose of this thesis is to investigate MOF coating effect and the shape effect of Pd nanocrystals on hydrogen storage properties and to find effective hydrogen storage materials at ambient temperature and pressure.

Hydrogen storage Properties of Pd cubes covered with HKUST-1

The author synthesized the Pd cubic nanocrystals exposed with {100} facets hybridized with the MOF-HKUST-1 as a core@shell structure (Pd cube@HKUST-1). The hydrogen storage properties of Pd cube@HKUST-1 were evaluated by hydrogen pressure–composition (PC) isotherms, in situ powder X-ray diffraction (XRD) and in situ solid-state ^{2}H NMR measurements. By coating Pd cubes with HKUST-1, a remarkable change in absorption properties occurs, with a 74% increase in hydrogen storage capacity for the Pd. Furthermore, the presence of the HKUST-1 coating also causes an enhancement in the kinetics of hydrogen storage. There enhanced hydrogen storage properties in Pd are MOF coating effect.

In situ Studies of Shape-dependent Pd Nanocrystals on Hydrogen Storage Properties

Compared to Pd bulk, it is known that Pd nanocrystals absorb less amount of hydrogen. But the nanoparticles exhibits high surface atomic ratio and high selectivity in catalysis of hydrogenation. Based on this, the author investigated the shape effect of Pd nanocrystals on hydrogen storage by Pd octahedral and cubic nanocrystals exposed with {111} and {100} facets, defined as Pd octahedrons and cubes, respectively. Because some recent studies have been mainly carried out to investigate the catalytic behaviors of different morphologies, but there are no reports about how the shape of the nanocrystals may affect the hydrogen storage properties of Pd. In this thesis, it is the first time to investigate the hydrogen storage properties of shape-controlled Pd nanocrystals. The hydrogen storage properties have been investigated by hydrogen pressure–composition (PC) isotherms, in situ powder X-ray diffraction (XRD) and in situ solid-state 2H NMR measurements. As a result, the octahedrons can absorb the same amount of hydrogen as the cubes, but the kinetics of absorption change with shape. The octahedrons with {111} facets exhibited rapid kinetics for hydrogen storage, compared to the cubes with {100} facets, originating from the differences in hydrogen diffusion pathway. In addition for the first time, the state of 2H in the solid-solution phase by in situ solid-state 2H NMR measurement was detected. These new findings provide clues not only for the development of effective hydrogen-storage materials but also for clarification of the catalysis mechanism associated with hydrogen and Pd nanocrystals.

HKUST-1 coating and Pd shape effects on hydrogen storage of Pd nanocrystals

The hybridization of Pd octahedrons coated with HKUST-1 has been investigated to compare with the hydrogen storage properties of Pd cube@HKUST-1 and understand the MOF coating effect. As a result, Pd octa@HKUST-1 absorbs larger amount of hydrogen than bare Pd octahedrons. In addition, the speed of Pd octa@HKUST-1 hydrogen absorption is faster than bare Pd octahedrons. Taking consideration into MOF coating effect, Pd octahedrons and cubes after coated with HKUST-1 absorbed larger amount of hydrogen than bare Pd nanocrystals. To study the mechanism of enhanced hydrogen storage capacity, the electronic state of Pd nanocrystals before and after coated with HKUST-1 has been investigated by X-ray photoelectron spectroscopy (XPS) measurement. The XPS spectra of Pd nanocrystals@HKUST-1 suggest that the electronic states of Pd nancrystals@HKUST-1 differ from those of bare Pd nanocrystals and pure HKUST-1 and that the electrons in the Pd nanocrystals are slightly transferred to the HKUST-1. This electron transfer may be responsible for the increased number of holes in the 4d band of Pd nanocrystals with the HKUST-1 coating, resulting in the enhanced hydrogen storage capacity in Pd after HKUST-1 coating. In addition, the shift of Pd 3d binding energies from Pd octahedrons to Pd octa@HKUST-1 was smaller than that from Pd cubes to Pd cube@HKUST-1. Moreover, compared the Cu 2p binding energies of the Pd octa@HKUST-1 and cube@HKUST-1 with pure that of HKUST-1, which of Pd octa@HKUST-1 showed more Cu^{2+} satellite than Pd cube@HKUST-1. This suggests that there is less partial reduction of Cu^{2+} in Pd octa@HKUST-1, maybe originating from more HKUST-1 weight ratio. Taking consideration into Pd 3d and Cu 2p binding energies, maybe less charge transfer occurred from Pd to HKUST-1 in Pd octa@HKUST-1 than that in Pd cube@HKUST-1, which may lead to relatively lower hydrogen-storage capacity in PC isotherms. Furthermore, the speed of hydrogen absorption in Pd nanocrystals coated with HKUST-1 also exhibits faster than bare Pd nanocrystals. Considering shape effect of Pd nanocrystals, the hydrogen storage capacity was almost the same between Pd octahedrons and cubes. The speed of Pd octahedrons was faster than that of Pd cubes. However, Pd octa@HKUST-1 absorbed less amount of hydrogen than Pd cube@HKUST-1, the speed almost the same. Because of the scarcity and expense of palladium, the findings are of limited direct practical value in the context of hydrogen storage. However, they show what is possible and may well inspire others to make progress on the storage problem using a less precious material.

In situ synthesis of PdCu bcc alloy from Pd cube@HKUST-1 under hydrogen gas

A dynamics synthesis of PdCu bcc alloy has been recorded through in situ XRD patterns at the BL02B2 beam line at SPring-8 during the thermal decomposed Pd cube@HKUST-1 under H2 gas pressure of 101.3 kPa at 773 K in 5 min. It is the first report that ordered PdCu bcc alloy can be synthesized by Pd nanocrystals hybridization with MOF. The ordered PdCu bcc alloy is expected to be high performance catalyst for hydrogenation reaction due to high hydrogen permeability. It has the potential to resist sulfur poisoning by hydrogen sulfide in hydrogen purification.